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SPECIFIC HEAT OF WATER VAPOR AT HIGH TEMPERATURES DERIVED FROM EXPLOSION EXPERIMENTS

BY

E. D. EASTMAN

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THE SPECIFIC HEAT OF WATER VAPOR AT HIGH TEMPERATURES DERIVED FROM EXPLOSION EXPERIMENTS[1]

By E. D. Eastman[2]

INTRODUCTION

There are three researches upon the specific heat of water vapor by the method of explosion that are sufficiently advanced in technique and suitable in plan to justify careful study of their results, with the double purpose of fixing the best available experimental values and indicating the attainable accuracy of the method. These three researches comprise the work of Pier[3], Bjerrum[4], and Siegel.[5] The work of earlier date than Pier's suffers from obvious inaccuracy of measurement, while the experiments more recent than Siegel's, such as those of Womersley[6], of Bone and his collaborators[7], and of Maxwell and Wheeler,[8] are for the most part not well designed for the accurate determination of the heat capacities in question. Some of the errors to which they are especially subject have been discussed by David[9] and by David and Thorp.[10]

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1 The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6337."

2 Consulting physical chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, Calif.

3 Pier, Mathias, Die Spezifischen Wärme von Argon, Wasserdampf, Stickstoff und Wasserstoff bei sehr hohen Temperaturen: Ztschr. Elektrochem., vol. 15, 1909, p. 536.

4 Bjerrum, Niels, Die Dissociation und die Spezifische Wärme von Wasserdampf bei sehr hohen Temperaturen nach Explosions versuchen: Ztschr. phys. chem., vol. 79, 1912, p. 513.

5 Siegel, Wilhelm, Untersuchungen von Gasgleichgewichten und spezifischen Wärmen nach der Explosions methode: Ztschr. phys. chem., vol. 87, 1914, p. 641.

6 Womersley, W. D., The Specific Heats of Air, Steam, and Carbon Dioxide: Proc. Roy. Soc. (London), vol. A - 100, 1921, p. 483.

7 For example, Newitt, Dudley M., Gaseous Combustion at High Temperatures. Part X. The Co-Volume Corrections, Maximum Temperatures, and Dissociation of Steam and Carbon Dioxide in Explosions: Proc. Roy. Soc. (London), vol. A-119, 1928, p. 464.

8 Maxwell, G. B., and Wheeler, R. V., The Pressure Produced on Inflammation of Mixtures of (a) Carbon Monoxide and Air, (b) Hydrogen and Air in a Closed Spherical Vessel: Jour. Chem. Soc. London, 1928, pp. 15-21.

9 David, W. T., The Dissociation of Carbon Dioxide at High Temperatures: Nature, vol. 120, 1927, p. 157.

10 David, W. T., and Thorp, B. H., The Pressures Developed in Gaseous Explosions: Nature, vol. 121, 1928, p. 420.

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In a previous report upon this subject[11] it was pointed out that Pier's results can be used with greater confidence than either Siegel's or Bjerrum's. The latter observers worked in a range of temperature where the dissociation of hydrogen might have an appreciable effect. In Pier's experiments this factor could not have been large. More important in influencing the choice of data, however, is the fact that Pier's may be recalculated, relative to argon, in such a way as to eliminate largely many of the errors that might be present in the direct results. These recalculated data appear to be free from any large error not characteristic of the method itself, and are to be regarded as the present standard values in their temperature range.

Nevertheless there are a number of reasons for consideration and recalculation of the data of Siegel and Bjerrum. In the first place, they have been widely quoted and used without a proper understanding as to the exact significance of their direct results. This is partly due to the fact that Siegel's individual values are not given in his article,[12] and Bjerrum applies a questionable correction for heat loss in the calculation of his. The values as published do not agree well with each other, nor with the values based upon Pier's measurements, nor with the figures adopted by Partington and Shilling[13] and reproduced in International Critical Tables, which are based in part upon Siegel's measurements. It is therefore desirable to make their actual results available. Secondly, as their upper limit of temperature exceeds Pier's by several hundred degrees the incorporation of their data with those of lower temperature, should it prove feasible, would be desirable. And, thirdly, it is urgent that all available information be applied in an effort to resolve an apparent difficulty with respect to the limiting heat capacity approached at these temperatures. Ordinarily there are ascribed to triatomic molecules but three vibrational degrees of freedom, placing a normal limit of about 14 calories upon C_p. All of the above discussed values exceed this limit. Thus at 2,500° K. the recalculated data of Pier lead to a value of 16.7 calories. Partington and Shilling give C_p at this temperature as 15.47. The corresponding values of $\bar{C}_v$ (mean specific heat at constant volume) of Siegel and Bjerrum are also above the theoretical value, Bjerrum's approaching it more closely than any of the others.

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11 Eastman, E. D., Specific Heats of Gases at High Temperatures: Tech. Paper 445, Bureau of Mines, 1929, 27 pp.

12 Siegel's results are represented in his paper by an equation in T^5 for the mean specific heat between 0° and T°K. This equation is based partly upon results at lower temperatures and has been influenced by them, so that in the range of the explosions the equation does not closely follow the actual direct results for heat capacity, upon which it purports to be based. By chance this equation follows closely over a part of its range, the values obtained from Pier's results relative to argon. The remark made in the former paper (ref. 11) that the equation is valueless, was based partly on these considerations partly on the uncertainties as to dissociation, and partly on a statement of Partington and Shilling (ref. 13, p. 130) as to the course of the equation.

13 Partington, J. R., and Shilling, W. G., The Specific Heats of Gases: London, 1924, 252 pp. The values of $\bar{C}_v$ do agree well in this case with Siegel's equation, and with the best values in this temperature range as adopted in reference 11; the values of C_p do not correspond, however, with those of the latter reference, the difference evidently arising in transposing mean to true specific heats, a slight difference in slope in the former evidently producing large variations in the latter.

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Following these ideas this report is devoted to a study of the above data. The first stage comprises a comparison of the direct results, which are not given in any of the original articles, of all three observers as obtained by calculation from their primary observations. The possible effect of the dissociation of hydrogen and water is next considered. This is followed by a discussion of possible inherent errors of the explosion method and by some remarks concerning theoretical possibilities leading to high specific heats.

CALCULATIONS

The calculations presented here fall into three groups. The first of these concerns the apparent heat capacity, as obtained from observations of the pressure rise during explosion of "small-gas" containing admixtures of certain diluent gases (and in some cases excess water vapor) in varying amounts. The formula that is applied is

$$\bar{C}_{v,H_2O}^{291,T} = \left[Q/(T-T_1) - \sum \underline{m}_i \; \bar{C}_{v,i}^{291,T} \right] /(1 + m_{H_2O}). \qquad (1)$$

In this equation, $\bar{C}_{v,H_2O}^{291,T}$ represents the mean molal heat capacity of water vapor between the initial temperature of 291° K. of the explosive mixture and the final maximum temperature, T° K. Q represents the heat absorbed by the products of combustion over the indicated temperature interval. In these calculations Q is taken as 57,530 calories, the heat of formation of 1 mol of water at constant volume and 291° K. This assumes that there are no heat losses of any kind during the explosion. The symbol $\underline{m}$ represents the number of mols of added diluent gas per mol of water formed in the explosion, subscripts being used to distinguish the separate gases; m_i is thus used to represent some particular diluent and m_{H_2O} the number of moles of water additional to that produced by the explosion. $\bar{C}_{v,i}^{291,T}$ represents the mean molal heat capacity of a diluent gas in the explosion. Values of the latter quantity used here for hydrogen and nitrogen are taken from the curves of Figure 2 of the former paper.[14] For argon the value 3R/2 was used at all temperatures. The final temperature, T, is calculated with the aid of the gas laws from the measured temperature, T_1, and pressure, P_1, before explosion and the final measured pressure, p. The contraction on burning must also be allowed for, the required relation being

$$T = c\, T_1\, p/p_1. \qquad (2)$$

In this equation $\underline{c}$, the "contraction" factor correcting for the change in number of molecules during reaction is

$$c = \frac{1.5 + \sum m_i}{1 + \sum m_i}. \qquad (3)$$

14 See reference 11.

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The data treated in this way include the high temperature (2,100°K. or higher) results of Pier in three series of experiments and the results of all the experiments of Siegel and Bjerrum in which excess hydrogen was present. The results are collected in Table 1, which includes also a partial summary of conditions indicating the formulas of the admixed gases, and the approximate initial pressure in each run.

Table 1. - Uncorrected heat capacities between 291° and T°K.

A. EXPERIMENTS OF PIER

Exp. No.	Added gases	Initial pressure (atmospheres)	Final temp., T° K.	291,T $\bar{C}_{v,H_2O}$ calories
166	H_2,H_2O	1	2104	8.73
167	do.	1	2290	9.03
168	do.	1	2523	9.68
161	N_2,H_2,H_2O	1	2190	8.99
162	do.	1	2417	9.41
163	do.	1	2598	9.94
144	A,H_2,H_2O	1	2620	9.94
145	do.	1	2606	9.88
146	do.	1	2599	9.84
147	do.	1	2382	9.13
148	do.	1	2426	9.30
149	do.	1	2369	9.08
150	do.	1	2155	8.47
151	do.	1	2312	1/ 8.84
152	do.	1	2248	1/ 8.70
153	do.	1	2338	1/ 8.90
	B. EXPERIMENTS OF SIEGEL			
71	H_2	2	2467	9.28
72	do.	2	2655	9.47
73	do.	2	2195	8.99
74	do.	2	2882	9.89
75	do.	1	2478	9.43
76	do.	1	2701	9.59
77	do.	1	2866	10.04
78	do.	1	2236	9.04
79	do.	1	2808	9.84
64	do.	0.2	2641	11.15
65	do.	0.2	2241	12.50
66	do.	0.2	2566	11.74
68	do.	0.2	2516	12.17
70	do.	0.2	2966	12.80
	C. EXPERIMENTS OF BJERRUM			
40	H_2	0.15	2578	13.45
38	do.	0.15	2718	13.57
30	do.	0.15	2868	13.49
51	do.	0.15	2928	14.11
29	do.	0.15	3103	14.50

1 The initial temperature corresponding to these values is 344°K.

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Heat Capacities Corrected for Assumed Dissociation of Hydrogen

The second group of calculations involves the same experiments that supply the material of Table 1, but is carried out on the assumption that equilibrium is reached in the dissociation of hydrogen and considering also the dissociation of water itself. In all of these experiments hydrogen was added in excess of the theoretical amount, with the intention of suppressing the dissociation of the water. As the temperature attained in some of the experiments was quite high, it is not apparent that the amounts of excess hydrogen were sufficient to accomplish this purpose. Accordingly this phase of the question was included in all calculations. It was found, however, that in every case the claim of the experimenter is substantiated, as the effects of the dissociation of water, assuming equilibrium to be reached, proved negligibly small. Explanation of the method of correcting for this dissociation will not be given in detail, since it may be inferred from the somewhat simpler example of hydrogen which is about to be discussed.

There are two ways in which the dissociation of the excess hydrogen affects the calculation of the heat capacity of the water. First, it affects the contraction factor c of Equations 2 and 3, and hence the calculated temperature of explosion. As the amount of dissociation and the explosion temperature are mutually dependent they must be calculated simultaneously by a series of successive approximations. The procedure is to adopt as a first approximation an explosion temperature obtained from Equation 2 with c unchanged. The amount of dissociation at this temperature is calculated from the corresponding equilibrium constant and the partial pressure of hydrogen in the explosive mixture at the instant of maximum pressure.[15] By changing the factor c to allow for this dissociation, a new explosion temperature is calculated. This temperature is too low, due to over-correction, where the original one is too high. By repetition of the calculation employing the last corrected temperature, the actual explosion temperature and amount of dissociation are finally approached as closely as desired. With the amount of dissociation fixed it is then possible to make the second correction, which relates to the heat absorbed in the dissociation (assumed to occur at the explosion temperature). This heat must be subtracted from Q in Equation 1 in calculating $\bar{C}_v$.

The detailed methods of these calculations need not be given, but the equilibrium and thermal data employed in them will be recorded. The value of ΔE for the reaction

$$H_2 = 2H \qquad (I)$$

15 The explosion pressure is not recorded in the papers of Pier and Siegel. It has been calculated by Equation 2 from their assumed explosion temperatures. In these calculations the initial pressure in Pier's experiments was also assumed to be 1 atmosphere.

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is obtainable from the measurements of Bichowsky and Copeland[16] and the calculations of Richardson and Davidson[17] based upon spectroscopic data. In agreement with them, the various thermal quantities pertaining to Reaction I required in this work have been taken as ΔE_0 = 4.46 volts equivalent = 102,930 calories; ΔH_{298} = 103,500 calories; ΔH_0 = 102,540 calories; ΔE_{2500} = 103,400 calories. As ΔE is not greatly affected by temperature, the last value suffices for use at the temperature of explosion in any of the experiments.

The free energy of Reaction I has been calculated by Giauque from accurate spectroscopic data, in conjunction with ΔE_0 as given above, at temperatures up to 5,000° K. Values of $-\log K$ at 2,000, 2,500, and 3,000° K. have been very kindly supplied by him in advance of publication. The preliminary values, subject to slight corrections, are 5.539, 3.173, and 1.573. These equilibrium constants have been plotted as log K vs 1/T. Linear interpolation on this plot supplied the values of K required above. The accuract of these values is supposed to depend primarily upon the accuracy of ΔE_0. This corresponds to about 25 per cent in K at 2,000° and 17 per cent at 3,000°. It is interesting to note that a free energy equation

$$\Delta F^0_T = 102,540 - 3.45T \ln T + 0.00045T^2 - 0.712T$$

based upon values of entropy at 298° K., again supplied by Giauque as S_{H_2} = 31.25, S_H = 27.4, together with ΔH_0 above and the specific heat equations given previously,[18] very closely parallels the curve mentioned above and might be used equally well.

The specific heats of water calculated on the above assumptions are exhibited in Table 2, which includes the same experiments as Table 1, with the exception of Pier's experiments 151, 152, and 153.

16 Bichowsky, F. R., and Copeland, L. C., The Heat of Formation of Molecular Hydrogen: Jour. Am. Chem. Soc., vol. 50, 1928, p. 1315.

17 Richardson, O. W., and Davidson, P. M., Proc. Roy. Soc. (London), vol. A-123, 1929, p. 466.

18 See reference 11.

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Table 2. - Heat capacities calculated from experimental data, assuming equilibrium in the dissociation of hydrogen

A. EXPERIMENTS OF PIER			B. EXPERIMENTS OF SIEGEL			C. EXPERIMENTS OF BJERRUM		
Exp.	Final temperature, T°K.	$\bar{C}_{v,H_2O}^{291,T}$	Exp.	Final temperature, T°K.	$\bar{C}_{v,H_2O}^{291,T}$	Exp.	Final temperature, T°K.	$\bar{C}_{v,H_2O}^{291,T}$
166	2103	8.59	71	2461	8.87	40	2545	12.08
167	2286	8.74	72	2642	8.83	38	2669	11.93
168	2512	8.78	73	2193	8.85	30	2787	11.35
161	2190	8.91	74	2854	8.91	51	2834	12.04
162	2414	9.27	75	2469	8.87	29	2956	12.08
163	2591	9.61	76	2680	8.65			
144	2613	9.48	77	2829	8.74			
145	2600	9.44	78	2233	8.77			
146	2594	9.40	79	2777	8.70			
147	2380	8.88	64	2517	9.94			
148	2423	9.02	65	2235	11.97			
149	2367	8.93	66	2540	10.48			
150	2155	8.46	68	2495	11.12			
			70	2873	10.39			

Calculations Involving Corrections for Dissociation of Water and Hydrogen

The third set of data employed include experiments by Siegel and Bjerrum with nitrogen and argon, respectively, as diluents and with no excess hydrogen. In these experiments correction must be made for the dissociation of water vapor. The dissociation of hydrogen produces appreciable effect in some instances also, although it is always small compared to the correction for the water. Both corrections have been made in these calculations. The principle is the same as in the simpler case and need not be again explained. The required equilibrium constants were obtained from a graph based on the free energy equation given in another report[19] for the reaction

$$H_2 + 1/2\ O_2 = H_2O \quad (g). \qquad (II)$$

The equation for free energy is limited to temperatures below 2,500°K. on account of the limitations in the specific heat terms. Within this range equilibrium constants obtained from the equation are probably correct within about 25 per cent at all temperatures. At 3,000°K., to which it has been extended in this case, the error in the constant should not exceed 40 per cent. As the error in the calculated dissociation is less than in the constant, and as the corrections are usually not large, they are moderately accurate. The results of the calculations are shown in Table 3.

19 Eastman, E. D., The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide: Information Circular 6125, Bureau of Mines, May, 1929, 15 pp.

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Table 3. - Heat capacities corrected for dissociation of water and assuming equilibrium in the hydrogen dissociation

A. EXPERIMENTS OF SIEGEL, NITROGEN AS DILUENT, INITIAL PRESSURE 1 ATMOSPHERE

Exp. No.	Final temperature, T°K.	291,T $\bar{C}_{v,H_2O}$
80	2337	10.00
81	2505	9.92
83	2731	10.20
84	3092	10.55
89	2684	9.76
B. EXPERIMENTS OF BJERRUM, ARGON AS DILUENT, INITIAL PRESSURE 0.13 ATMOSPHERE		
53	2565	14.10
54	2730	13.66
57	2815	13.16
56	2865	12.78
55	2925	12.98

Discussion of Calculated Values of Heat Capacity

Inspection of the specific heats in Tables 1, 2, and 3 reveals at once that the experiments of Bjerrum, at 0.16 atmosphere, and of Siegel at comparable pressures, are affected by large errors. They are not in agreement with each other, nor with any of the other measurements at higher pressures. The effect of dissociation of hydrogen, as seen in the tables, is not sufficient to bring them into agreement. There appears to be no way to utilize these measurements. Bjerrum's attempt to do so by making arbitrary corrections for heat losses must be disregarded, and his equation, regardless of how nearly correct it may be, has no adequate experimental foundation in the upper temperature range. Such inferences as may be drawn from these measurements will be brought up in the later discussion.

The measurements at initial pressures in the neighborhood of 1 and 2 atmospheres are reasonably consistent. The uncorrected results of Pier and of Siegel in Table 1 are plotted in Figure 1. The three series of Pier show no significant differences among themselves and have not been separately distinguished on the plot. Siegel's values at 2 atmospheres lie uniformly slightly below his corresponding measurements at 1 atmosphere. As the difference, though probably a real effect, is little more than the possible error, these points are not given distinctive marks either. At only one point, near 2,600°K., does appreciable lack of agreement between the two observers appear. Siegel's measurements should undoubtedly be given greater weight than Pier's, as far as the direct values are concerned.

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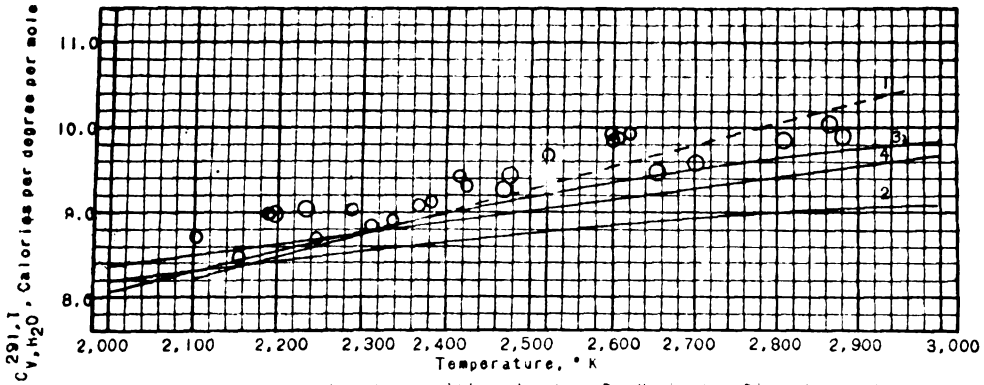

Figure 1.- Uncorrected heat capacities of water: Small circles, Pier; large circles, Siegel; curve 1, Pier, relative to argon; curve 2, theoretical; curve 3, from Siegel's equation; curve 4, from equation 4

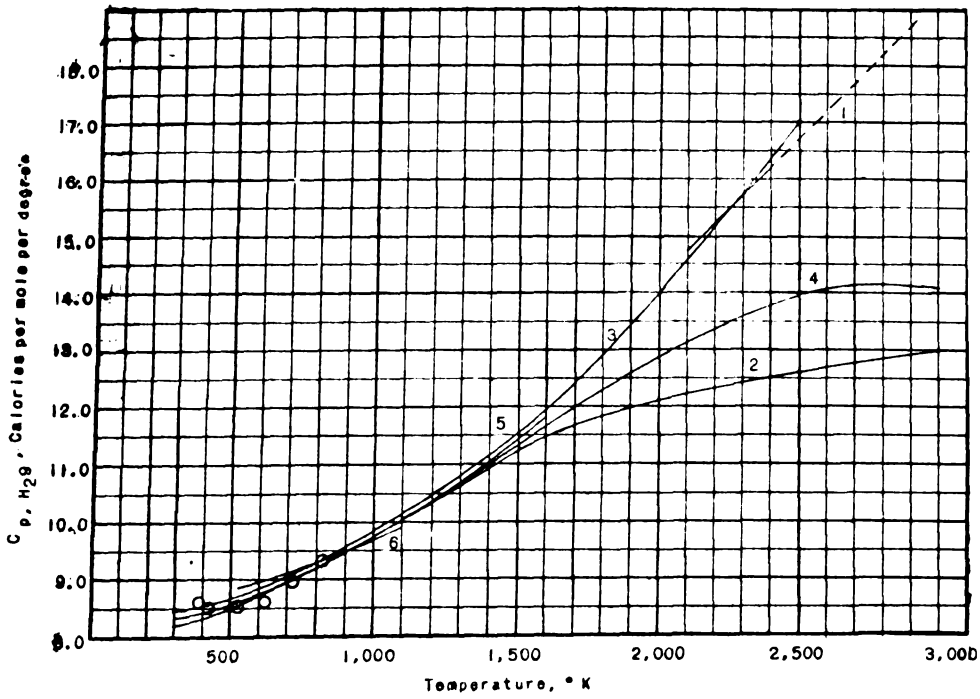

Figure 2.- Comparison of equations for "true" heat capacity. Measurements: Curve 1, Pier, relative to argon; curves 5 and 6, Holborn and Henning; circles, Knoblauch. Comparison equations: Curve 2, theoretical; curve 3, final equation of reference 9; curve 4, from equation 4

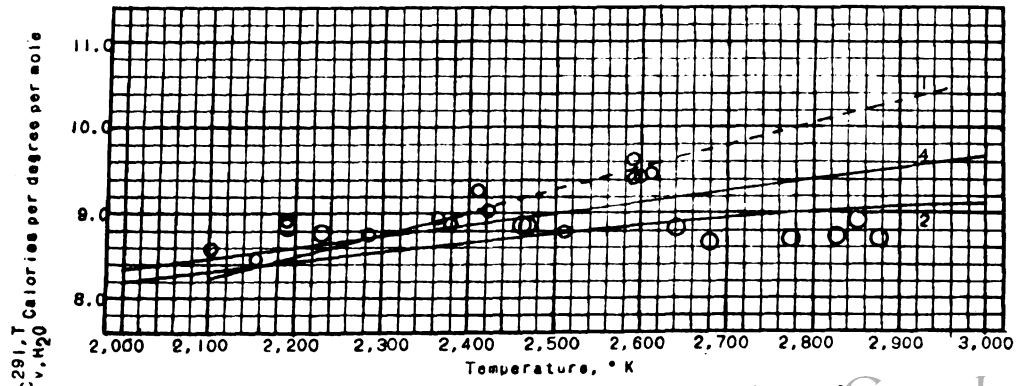

Figure 3.- Heat capacities corrected for assumed dissociation of hydrogen. (Designation of points and curves as in Fig. 1)

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For comparison with the direct results in Figure 1, several curves are also shown. Thus the values relative to argon deduced previously[20] from Pier's work are given by the solid portion of curve 1. An extrapolation to cover the wider temperature range considered here is comprised in the dotted portion of this curve. This part of the curve has no experimental basis, yet may lie close to the true values, as discussed below. Curve 2 is based upon a theoretical curve for C_p derived by Giaugue by applying certain optically determined frequencies in the Planck-Einstein equation for vibrational specific heats. The assignment of frequencies is uncertain, and the calculations therefore are purely preliminary in character. The form of the curve is typical, however, of that to be expected, and it will be used as such. The later discussion will center principally about the relative experimental validity of these two curves, recognizing that both are subject to some modification. Curve 3 of the Figure 1 is calculated by transforming Siegel's equation. This equation may be approximately valid. It does not, however, follow closely the results in the region that it was intended to represent. Moreover it is complex in form, and according to Partington and Shilling gives a maximum in C_v (true specific heat) of 13.25 near 2,500° K., with rapidly falling values at higher temperatures. It will not be further discussed. Another curve, numbered 4 in the figure, closely parallels it. Its equation is simpler in form than either Siegel's empirical one, or the Planck-Einstein type. It is derived from the following:

$$C_p = 8.32 - 6.53 \times 10^{-4} T + 2.70 \times 10^{-6} T^2 - 6.145 \times 10^{-10} T^3. \qquad (4)$$

Equation 4 nowhere within its range of 300 to 3,000° K. very much exceeds 14 calories and closely represents the lower temperature results.

In order to fix the significance of these curves as to true specific heats, they are shown, with the same designations, in this form in Figure 2, which includes also the experimental results at lower temperature and the final curve of the former paper.[21]

The data of Table 2 calculated on the assumption of equilibrium in the dissociation of hydrogen are shown in Figure 3. This figure includes also the principal curves of Figures 1 and 2. It is apparent that at the higher temperatures the agreement of the corrected points with the optical curve (number 2) is close. It is equally apparent, however, that to obtain complete agreement of the measured points with this curve, the assumption respecting dissociation of hydrogen is not enough. Such agreement might be obtained only by the further assumption of relatively large heat losses, or other errors, at the lower temperatures, diminishing rapidly as the explosion temperature increases and becoming inappreciable at the highest temperatures. Since there is evidence supporting such an assumption in a qualitative sense, it becomes of much importance to test it quantitatively. For this purpose a consideration of the nature and possible magnitude of some of the errors of measurement is necessary.

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20 See reference 11.
21 See reference 11.

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Possible Errors of Measurement

Heat Losses.- There are several ways of approaching the study of heat losses. From the form of the pressure-time record of the explosions an estimate of the order of magnitude of the losses may be made. The data under discussion have not been treated by the author from this standpoint. In the explosion of hydrogen and chlorine, however, Wohl[22] estimates that the loss is negligible at temperatures higher than 1,900° K.

The effect of the temperature of explosion upon its duration is well indicated by these records in both the chlorine and oxygen explosions. The greatly decreased interval accounts for the reduction of losses which is always found at the higher temperatures. Pier considered that heat losses were negligible above about 2,400° K.

A second indication is found in the comparison of the directly calculated values with those relative to argon. This comparison is most reliable at about 2,300° K. At this temperature, the total loss including any effect of the dissociation of hydrogen, produces a maximum error of 3 or 4 per cent in the heat capacity of water. This assumes the accuracy of the relative values, which will be discussed later.

Again the heat losses are strongly dependent upon pressure. Bjerrum and Siegel assumed the percentage heat loss to be inversely proportional to the initial pressure. This assumption is unlikely to be closely correct. Using it, however, Siegel calculates that his losses at 1 and 2 atmospheres initial pressure were small enough to neglect at all temperatures in his work.

Concerning the losses by radiation, the direct measurements of David[23] are available. The conditions of his experiments do not duplicate the present ones exactly, but are roughly comparable. He finds a loss of 0.5 per cent during the explosion of hydrogen and air when temperature was 2,400° K and 1.3 per cent at 1,580° K. In the bomb used by Pier and Siegel the loss should be smaller than this.

Equilibrium Effects.- Absence of complete equilibrium at the time the maximum pressure is reached offers a possibility of error on the side of high specific heats. If, for example, the reaction is incomplete at the time the maximum pressure is developed, such values will result. David and Thorp[24] give experimental estimates varying from 3 to 10 per cent of minimum values of the percentage of unburned gas at maximum pressure in hydrogen-oxygen-nitrogen mixtures containing no excess hydrogen. With excess hydrogen this percentage must be much reduced. These authors consider, however, that even with large excess of hydrogen large effects may still remain, under the conditions of their experiments, approaching zero with increasing initial pressures. It appears probable that the cooling of

22 Wohl, Kurt, Die Dissoziation von Chlor und Wasserstoff in die Atom: Ztschr. Elektrochem., vol. 30, 1924, p. 49.

23 David, W. T., Radiation in Gaseous Explosions: Trans. Faraday Soc., vol. 22, 1926, p. 273.

24 See reference 10.

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the gases at the surface of the bomb is responsible in part for this effect. Pier and Siegel had much more favorable conditions than David and Thorp in this respect and the error should be much reduced in their experiments. Wohl found evidence of "after-burning" of this kind only with much diluted mixtures and never when excess hydrogen was alone present. Even in the mixtures in which the effect appeared it was appreciable only below 2,400° K. and was only about 0.75 per cent at 1,955° K.

It seems probable, also, that after-burning is mainly responsible for the large losses in the experiments of Siegel and Bjerrum at low pressures. As the change in apparent specific heat between 1 and 2 atmospheres is so small, however, it seems safe to conclude that at these pressures the effect is very largely eliminated in the measurements under discussion. It may nevertheless influence appreciably the experiments of Siegel with nitrogen as diluent listed in Table 3, as well as all of the low-pressure measurements.

Other possible sources of error which fall under the heading of "equilibrium effects" may be mentioned. The formation during the period of reaction of activated molecules which are unstable at the maximum temperature but do not all decompose until after the maximum pressure is reached, would give rise to high apparent specific heats. An effect of this kind is suggested by the results of David[25] on explosions of hydrocarbons, where the radiation was not simply a function of temperature, but was most intense before the highest temperature was developed. With explosions of hydrogen this was not the case; the presence of such effects remains therefore an unsupported possibility. A somewhat similar possibility, for which there is again no evidence, is the formation in the early stages of explosion of some unstable substance, such as H_2O_2, decomposing completely only after maximum pressure has been passed. The presence of such molecules should be revealed by the quality of the radiation during explosion, but to date this has not been studied.

Errors in Heat Capacities Calculated Relative to Argon

Most of the errors discussed above should be greatly reduced in the determination of relative heat capacities. The values obtained previously in this way from Pier's series of experiments with argon should be free from serious defects in principle, with the possible exception of specific differences between argon and water in their influence upon the rate and equilibrium of the explosion. There is a slight correction to the temperatures as plotted in Figure 6 of the former paper,[26] if hydrogen is assumed to dissociate, but it has little effect upon the calculated heat capacities. One source of small error, not inherent in the method but affecting Pier's experiments, is found in the necessity of correcting for differences in the initial temperatures of the experiments with excess water vapor as compared with those in the argon series. In the former calculations this correction was made by determining the composition of mixtures, keeping the same proportions of added gases, which would have produced the same final temperatures starting from 291° K. as were produced by the actual mixtures starting from 326° K.

25 See reference 23.
26 See reference 11.

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This method is preferable to the other possible one of assuming the change in temperature on explosion to be independent of the starting temperature, and taking the actual compositions with only slight changes, to reduce them to the standard mixture, for the construction of the curves for determining relative values. The latter method yields less consistent results than the former; it agrees reasonably well on the average over the whole range, but at 2,300° K. where the results should be most reliable gives heat capacities several per cent higher than the first method. There is little doubt of the greater reliability of the first method. Yet the necessity for this correction, together with the small number of experiments, makes imperative the restriction of the values to the mid-points of the range of temperature actually covered by the experiments. If the second method of correction is given any weight, it reduces the estimate of the heat losses obtained by comparing the directly calculated heat capacities with the relative.

Evidence that Hydrogen does not Dissociate

The collective evidence adduced in the preceding sections, although no single point of it is alone completely convincing, tends rather uniformly to the conclusion that the heat losses which undoubtedly affect the direct calculations have been amply corrected for in the relative determinations. So far as the experimental evidence at present available is concerned, the discrepancy, although not large, seems real between the experimental values of Figures 1 and 3 and our type curve (number 2 in the figures), at least in part of the temperature range. This makes the agreement at the higher temperatures of the latter curve with calculations assuming dissociation of hydrogen appear fortuitous.

It would thus be desirable to have independent evidence as to the actual extent of this dissociation in these explosions. Here again there is nothing decisive available. It may be pointed out, however, that had the dissociation occurred appreciably, its effect should be rather different in the three series of Pier with argon, nitrogen, and hydrogen, respectively, present in large excess. Actually the three do not differ significantly, as shown in Figure 1. A similar consideration applies to Siegel's series with nitrogen and Bjerrum's with argon. These measurements are not as largely affected by the hydrogen dissociation as are the other comparable experiments. Had the dissociation occurred in the latter, the apparent values should lie above the nitrogen and argon series. Actually they do not. This argument is of somewhat lessened force in these last instances because of a possible complication from after-burning.

These are the only experimental leads. Inadequate though they are, they consistently indicate that the dissociation of hydrogen if it occurs appreciably during these explosions, at least does not reach the full equilibrium value. This is not necessarily in conflict with the results in the hydrogen-chlorine explosions, where the dissociation of hydrogen does occur, because the mechanism of the latter reaction is known to involve the formation of monatomic hydrogen.

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Theoretical Possibilities of High Specific Heats

Since the evidence is not clear that the high apparent specific heat is due to errors or to the dissociation of hydrogen, it is in order to consider the possibility of a real effect. Such an effect could be present if there are two forms of water molecules, with an energy difference of appropriate magnitude (less than 1 volt-electron). The necessity of an assumption of this kind has not appeared as yet in any other connection. Foote and Mohler[27] report a doubtful resonance potential for water vapor at 7.6 volts, which even if it exists is too high to be of interest here. Electron jumps do not occur in the water molecule, as far as the analyses now available of the spectral data are concerned. These analyses are perhaps incomplete, and it is of interest that in the OH molecule, bands due to which are obtained in the spark discharge in water vapor, there are two electronic states with about 4.00 volts[28] difference in level. It is not unreasonable to expect a similar level (possibly a lower one) in the water molecule. Its existence, or that of any other sort of excited state, remains, however, an unsupported hypothesis.

The possibility of more than three degrees of "internal" freedom of triatomic molecules also requires assumptions which have not as yet proved necessary in other considerations, although they follow from some of the cruder chemical models. As long as the molecule is regarded merely as an assemblage of three massive points mutually interacting under appropriate laws of force,[29] three degrees of freedom is the maximum number required to describe the possible oscillations of the atoms. There appears to be no justification of Eucken's[30] assumption that four are necessary in the case of three atoms whose normal configuration is linear. Indeed with a strict constraint of this kind, the number would obviously be reduced to two. If, however, the model comprising three massive point centers of force is displaced by one in which the atoms have the tetrahedral structure of electrons employed so often in chemical considerations, and are joined by electron pairs which constitute localized forces or bonds, three coordinates may no longer be enough to fix the internal energy of the molecules. Additional coordinates, corresponding to an increased number of degrees of freedom, might then be required to specify the orientations of the tetrahedra, before the potential energy is determined. A heat capacity (at constant volume) much greater than 12 calories, in the absence of excited states, would apparently require some such assumption for its explanation. This is one of the reasons for the interest in the present apparent discrepancy, although the water molecules would be less likely to show any such effect than some of the carbon compounds. The evidence at present is certainly not enough to establish any such hypothesis, and the present trend in quantum mechanics is away from such detailed models.

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27 Foote, Paul D., and Mohler, F. L., The Origin of Spectra: New York, 1922, p. 188.

28 Birge, Raymond T., International Critical Tables: Vol. 5, 1929, p. 415.

29 Deviations from Hooke's law are possible sources of high specific heats, but it is unlikely that they are of importance, since most of the molecules are in relative low vibration states.

30 Eucken, A., und Lüde, K. V., Die spezifische Wärme der Gase bie mittleren und hohen Temperaturen: Ztschr. physikal. Chem., Abt. B, Bd. 5, 1929, p. 439. Also Eucken, A., Zur Frage nach der Gestalt der Kohlensäure molekel: Ztschr. Physik, vol. 37, 1926, p. 714.

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CONCLUSIONS

The conclusions resulting from the considerations presented in the preceding may be stated as follows. Hydrogen apparently does not dissociate during explosions under the conditions discussed here to an extent closely approaching the equilibrium conditions. At temperatures above about 2,300° K. heat losses larger than 3 or 4 per cent do not occur in the experiments with initial pressures of 1 atmosphere or higher. In the neighborhood of 2,300 or 2,400° K. the values of $\bar{C}_{v,H_2O}$ as previously determined relative to argon remain the best founded experimentally, and their extrapolation approaches the best direct values up to 3,000° K.

None of the evidence leading to these conclusions is decisive. It remains possible that the curve of $\bar{C}_v$ plotted against T really conforms, for example, to curve 2 of Figures 1 and 3. All of the doubtful points concerning the actual curve seem to be susceptible of experimental resolution in well-conceived experiments. Until the results of such studies become available, those to whom the matter is of interest will no doubt prefer to make their own choices between such curves of C_p plotted against T as numbers 1, 2, and 4 of Figure 2. Number 1 has the advantage of following closely the best founded experimental values, and the disadvantage of exceeding the normally expected limit of heat capacity. Curve 2 conforms to the usual type and in certain ranges of temperature is close to the best values, but requires for complete justification two experimentally unsupported assumptions (relatively large heat losses at lower temperatures, which disappear at the higher, and the dissociation of hydrogen to the full equilibrium extent). Curve 4 of Figure 2 may serve as a compromise equation, since it fits the best data in the lower ranges and would be accounted for in the upper if a partial dissociation of hydrogen occurs. It is roughly correct as to type (within its range), does not seriously exceed the theoretical limit, and is of convenient analytic form.

SUMMARY

Calculations have been made of the apparent heat capacity of water vapor from several series of explosion experiments by Pier, Siegel, and Bjerrum, assuming no heat losses, and that hydrogen doesnot dissociate. The same data are then treated on the assumption that the dissociation of hydrogen reaches its equilibrium value, and some further experiments are calculated in which the dissociation of both water and hydrogen is allowod for.

The results of these calculations are compared with values given by the original authors, and others, based on the same data. It is shown that the latter values are not in fact representative of the experiments upon which they purport to depend.

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Comparison is also made with the values obtained by calculation relative to argon, and with those assuming the true C_p to approach its normal limit of 14 calories. It is shown that the dissociation of hydrogen is alone not onough to secure agreement of the directly calculated values with the latter at all temperatures, though it does so in the upper range. Complete agreement might be indicated only if the further assumption of considerable heat losses at the lower temperatures is made. The experimental evidence, while not decisive, indicates that no losses large enough to account for the difference were present, and is also unfavorable to an appreciable dissociation of hydrogen.

It is considered, therefore, that the values relative to argon possess at present the surest experimental foundation of any. The rise of C_p above 14 calories as deduced from these values, however, is not established, since a relatively small error in slope of $\bar{C}_v$ vs T might account for it, and curves consistent with the experiments in their most reliable range may be drawn that do not show this "excess" heat capacity. There is a possibility that the extrapolation of these values gives nearly correct results at the higher temperatures, in which case the excess is real.

Some of the theoretical possibilities leading to high specific heats are discussed, and it is pointed out that certain statements in the current literature attributing four degrees of vibrational freedom in the ordinary sense to particular forms of triatomic molecules are incorrect.

ADDENDUM

After the submission of the manuscript of this paper, the work of Wohl and von Elbe[31] in the same field was brought to the attention of the writer. Calculations analogous to some of those described in this paper have been made by these authors, who find agreement with the optically determined specific heat curve. Their work differs from the present investigation in the following particulars:

In the first place, Wohl and von Elbe cite experiments of their own, tending to show that in the explosion of dry mixtures of hydrogen and oxygen appreciable heat losses occur, while explosions of mixtures containing water-vapor are nearly without loss. On the basis of these experiments they give less weight to the results of Siegel than to those of Pier or Bjerrum. They are continuing the investigation of the effect mentioned. Until the completion of their studies, various questions must remain open. The explanations advanced by them (quenching of luminescence, or absorption ahead of the flame by the "cold" water-molecules) are plausible. If, however, they should have to be abandoned in favor of a differing surface effect, in the nature of uncomplete combustion or after-burning, in the wet as compared with dry mixtures, it might be found that the very large bomb employed by Siegel reduced the effect to negligible proportions in his experiments. There appears at present to be no compelling reason to distrust his results.

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31 Wohl, Kurt, and von Elbe, Günther, Der Einfluss des Wasserdampfes auf die Wärmestrahlung explodierender Gasgemische. Die spezifische Wärme des Wasserdampfes bei hohen Temperaturen: Ztschr. phys. Chem., Abt. B, vol. 5, 1929, p. 241.

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The second point of difference to be noted is found in the equilibrium data pertaining to the dissociation of hydrogen. It is believed that the figures employed in this work, which are from the calculations of Giauque, are more reliable than those used by Wohl and von Elbe. Comparison on this point will be made possible by the publication of his work in the near future by Giauque.

Thirdly, Wohl and von Elbe include in their calculations the dissociation of water into hydrogen and hydroxyl. Their calculations are based upon the data of Bonhoeffer and Reichardt,[32] whose paper escaped the attention of the writer. A study of their work, however, indicates that this dissociation can not as yet be treated with the accuracy desirable in the present connection. It is likely that at extreme temperatures the effect of this dissociation is appreciable. Qualitative considerations might be cited, however, which indicate that it is, over much of the temperature range considered here, not more important than the ordinary dissociation into hydrogen and oxygen.

A final comment concerning the high apparent values of the heat capacity of water should be made. From the viewpoint of Wohl and von Elbe, there are three sources of these high results in such work as Siegel's. These are the heat loss mentioned above, the dissociation of hydrogen, and the dissociation of water into hydrogen and hydroxyl. The calculations of the present paper, however, show very definitely that the assumption of all three of these effects is unnecessary. Thus, the hydrogen dissociation alone, if fully effective, is sufficient to account for the excess above theoretical specific heats. A partial contribution from each of the three causes remains possible, of course, and this possibility undoubtedly renders the excesses above the theoretical curve less significant.

32 Bonhoeffer, K. F., and Reichardt, H., Zerfall von erhitztem Wasserdampf in Wasserstoff und freies Hydroxyl: Ztschr. phys. Chem. Abt. A, vol. 139, 1928, p. 75.

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